

# Hydrodynamic Brownian motion of Rouse-Zimm polymer coils

Jana Tothova, Vladimir Lisy

Technical University of Košice, Slovakia

**Subject:** Long chains of particles (monomers, beads) in fluids – such as flexible polymers in solution

Motion of chains is driven by **thermal noise forces**.

**Main aim** of the work: more realistic description of the dynamics of polymers in solution than so far.

## **Motivation:**

Traditional theories of polymer dynamics are based on Einstein' theory of Brownian motion, valid only at  $t \rightarrow \infty$ .

Existing theories do not give a good description of experiments; some problems are unsolved for decades.

Current experiments go to very small time and length scales.

“Color” of thermal noise in fluids has been recently observed (Franosch et al., Nature 2011, Janaasch et al., PRL 2011) – very different from white noise, assumed in previous theories.

## **Background:**

A success depends on the existence of an idealized model giving a good description of real macroscopic systems.

Is there an ideal model for polymer chains?

(large or small parameters, ordering...)

The description of polymer dynamics can be idealized, since:

– the number of monomers in the chain is large,  $N \gg 1$

- relation  $E_1/E_2 \gg 1$ ,  $E_1$  ( $\sim 5$  eV) is the binding energy between the neighbor monomers,  $E_2$  ( $\sim 0,1$  eV) is the energy of all other interactions, so called volume interactions; there exists “linear memory“ along the chain
- any long chain is flexible and thus coiled in the solution

(e.g. DNA in the human chromosome is 1 m long while the cell nucleus has a diameter of  $10^{-6}$  m)

- only distances and times  $\gg$  atomic ones are considered;

*universal effects*, common for all chains, are studied (chemical details are neglected)



### Time scales

For the description of any experiment it is important to specify the considered time scales.

In case of polymer chains the time range is enormous:

from the microscopic origin of their motion to macroscopically observed phenomena.

*Characteristic times:*

- random forces characterized by the time of collisions of surrounding molecules with the chain particles,  $\tau_{coll} \sim 10^{-12}$  s.

Only for particles with dimensions  $\gg$  dimensions of molecules and times  $\gg \tau_{coll}$  we can consider the hits of molecules as a stochastic noise and the surrounding as a continuum.

In such approximation one can try to use the Langevin equation for a particle of mass  $m$  and radius  $R$ . Its projection to some direction, e.g.,  $x$ , is

$$m\dot{u}(t) + \gamma u(t) = \eta(t).$$

The noise is related to friction by the relation  $\langle \eta(t)\eta(t') \rangle = 2k_B T \gamma \delta(t - t')$ ,  $\gamma = 6\pi\eta R$ , if the friction force is  $\sim$  velocity  $u$  (Stokes force).

However, this equation is valid only in very limited conditions (long times, or short times and large densities of particles).

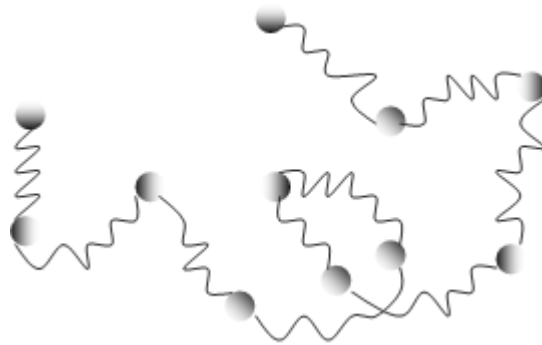
It does not work for particles with a density smaller or comparable to the density of solvent (freely floating in a fluid).

Due to this another characteristic time appears. Within the hydrodynamics this time is  $\tau_R = R^2 \rho / \eta$ .

– Langevin theory is applicable for times  $\gg \tau_R$ .

– At comparable or shorter times inertial and memory effects are important: for example, if  $R \sim 100$  nm,  $\tau_R \sim 10^{-8}$  s.

– The surrounding can be compressible; the compressibility can be neglected for times  $\gg \tau_{\text{sound}} = R/c$  ( $c$  – velocity of sound,  $\sim 1500$  m/s in water at room  $T$ ). For particles of radius  $R \sim 100$  nm is  $\tau_{\text{sound}} < 10^{-10}$  s.



## Existing models

Most popular – Rouse and Zimm models

Rouse (1953) – nonmoving solvent (the model works well for dense solutions)

[Should be called Kargin-Slonimskii-Rouse]

Zimm (1956) – hydrodynamic interactions are taken into account (motion of monomers affects other monomers through perturbation of the solvent flow; the model works for dilute solutions at long times)

## Existing problems

Significant discrepancies between the measured quantities and theoretical predictions (diffusion coefficient, dynamic structure factors and their cumulants, viscosity of solution, de Gennes'  $k^3$  law, ...) – unsolved for decades.

Although the basic ideas are clear, their formalization causes difficulties:

What is the real equilibrium distribution of the particles in the chain? (Usually it is assumed Gaussian, which determines also the forces between the particles.)

Is the chain really flexible?

How to take into account the motion of solvent?

How to describe the overlapping of the individual chain and between different chains?

Is there an internal friction in the chain?

The models are strictly nonlinear. The linearization gives rather good results, but still it is not substantiated.

....

We have changed the standard models coming from the observation that:

- The friction force cannot be the Stokes one.
- Then, due to FDT, also the random forces driving the particles should be changed. The particles are driven by a “colored” noise.

## Random force

We have considered 2 models of the random force:

1. The force that follows from the hydrodynamic theory of Brownian motion (for the first time experimentally detected by Franosch et al., Nature (2011) and Janaasch et al., PRL (2011))

$$\frac{\langle f(t)f(0) \rangle}{k_B T \gamma} = -\frac{1}{\tau} \sqrt{\frac{\tau_R}{\pi t}} - \frac{1}{2} \sqrt{\frac{\tau_R}{\pi t^3}}, \quad t > 0,$$

$\tau = M/\gamma$ ,  $M = m + m_s/2$   $m_s$  is the mass of the solvent displaced by the bead

2. Ornstein-Uhlenbeck random force (solution for  $mdv/dt$  of standard Langevin equation) – exponentially correlated noise.

In both cases the system shows memory – the friction force is a convolution of the acceleration (1) or velocity (2) with a memory kernel  $\Gamma(t)$ . The loss of memory is  $\sim t^{-1/2}$  (Model 1) or  $\sim \exp(-t/\tau)$  (Model 2).

The formal approaches are similar. Here we consider Model 1.

## Generalization of the Rouse model of chain dynamics

Equation of motion for the  $n$ th particle (projected on axis  $x$ ) is

$$m \frac{d^2 x_n}{dt^2} = f_n^{fr} + f_n^{ch} + f_n,$$

$x_n$  – radius vector of a particle of mass  $m$ ,  $f_n^{fr}$  – friction force,  $f_n^{ch}$  – force by other particles in the chain,  $f_n$  – random force.

Friction (Boussinesq force)

$$\vec{f}_n^{fr}(t) = -\gamma \vec{v}_n(t) - m_s \dot{\vec{v}}_n(t) - 6R\sqrt{\pi\rho\eta} \int_{-\infty}^t \frac{d\vec{v}_n}{d\tau} \frac{d\tau}{\sqrt{t-\tau}}$$

**Original Rouse model** (used to describe dense solutions and melts) **was**

- without the inertial term (overdamped motion), which leads to incorrect behavior at short times
- there was the Stokes force instead of the Boussinesq one
- and white Langevin force instead of  $f_n(t)$

**Motion of the whole coil: discrete variant of the model is solvable**

After summation of the equations of motion internal forces disappear and we obtain the equation for the center of mass  $MN$  of the coil,

$$MN \frac{d\upsilon_T}{dt} + \gamma N \upsilon_T + 6NR^2(\pi\rho\eta)^{1/2} \int_{-\infty}^t \frac{d\upsilon_T(\tau)}{d\tau} \frac{d\tau}{\sqrt{t-\tau}} = f,$$

$$x_T = \sum x_n / N, \quad f = \sum f_n, \quad \upsilon_T = \sum \upsilon_n / N$$

From here an equation follows for  $V_T \equiv dX_T / dt$ ,  $X_T(t) = \langle [x_T(t) - x_T(0)]^2 \rangle$  is the mean square displacement of the coil, also expressed through the velocity autocorrelation function  $\Phi_T(t) = \langle \upsilon_T(0) \upsilon_T(t) \rangle = (d^2/2dt^2) X_T(t)$  as

$$X_T(t) = 2 \int_0^t (t-s) \Phi_T(s) ds$$

$$f \rightarrow 2k_B T$$

$$X_T(0) = 0, V_T(0) = 0$$

Using the Laplace transformation  $\tilde{V}_T(s) = \mathcal{L}\{V(t)\}$  we find

$$\Phi_T(t) = \frac{k_B T}{MN(\lambda_2 - \lambda_1)} \left\{ \lambda_2 \exp(\lambda_2^2 t) \operatorname{erfc}(-\lambda_2 \sqrt{t}) - \lambda_1 \exp(\lambda_1^2 t) \operatorname{erfc}(-\lambda_1 \sqrt{t}) \right\}$$

$$\lambda_{1,2} = -(\tau_R^{1/2} / 2\tau) [1 \mp \sqrt{1 - 4\tau / \tau_R}]$$

$\tau = M/\gamma$  is the usual Brownian relaxation time

$\Phi_T(t)$  was = 0 in the original model, now at  $t \rightarrow \infty$  it contains

a long-time tail  $\sim t^{-3/2}$ :

$$\Phi_T(t) \approx \frac{k_B T}{2\gamma} \left( \frac{\tau_R}{\pi t^3} \right)^{1/2} \left[ 1 - \frac{3}{2} \left( 1 - \frac{6\tau}{\tau_R} \right) \frac{\tau_R}{t} + \dots \right]$$

Mean square displacement  $X_T(t) = \int_0^t V_T(\tau) d\tau$  (the measured quantity)

$$X_T(t) \approx (2k_B T t / N\gamma) [1 - 2(\tau_R / \pi t)^{1/2} + \dots]$$

In the main approximation we have the known result by Rouse

$$X_T(t \rightarrow \infty) \approx \frac{2k_B T t}{N\gamma}$$

At  $t \rightarrow 0$ , independently on the character of the random force,

$$X_T(t \rightarrow 0) \approx \frac{k_B T}{NM} t^2.$$

For **internal modes** we so far haven't an exact solution of the discrete model.

Approximate solutions have been obtained in the continuum approximation.

## Zimm model with hydrodynamic interactions (HI)

The inclusion of HI brings serious difficulties:

- One has to calculate the velocity of the solvent in the place of  $n$ th bead due to the motion of other beads,  $\mathbf{v}(\vec{r}_n)$ , and then to determine the friction force through  $d\vec{r}_n/dt - \mathbf{v}(\vec{r}_n)$
- To do this, the hydrodynamic equations for the solvent must be solved. The Navier-Stokes equation contains an additional force density reflecting the force from the beads on the solvent.
- The solution for  $\vec{v}(\vec{r})$  is expressed through a nonstationary Oseen tensor  $H_{\alpha\beta}(\vec{r}, t)$ ; this makes the problem nonlinear.

Equations of motion in the Fourier representation

$$\dot{r}_{n\alpha} = \int_{-\infty}^{\infty} d\omega r_{n\alpha}^{\omega} \exp(-i\omega t)$$

reads

$$-i\omega r_{n\alpha}^{\omega} = \psi_{n\alpha}^{\omega} (\gamma^{\omega})^{-1} + \sum_{\beta} \sum_{m \neq n} H_{\alpha\beta}^{\omega}(\vec{r}_n - \vec{r}_m) \psi_{m\beta}^{\omega},$$

where  $\psi_{n\alpha}^{\omega} = f_{n\alpha}^{ch,\omega} + f_{n\alpha}^{\omega} + m\omega^2 r_{n\alpha}^{\omega}$ ,  $\gamma^{\omega} = \chi[1 + \chi R + (\chi R/3)^2]$ , and  $\chi = \sqrt{-i\omega\rho/\eta}$  ( $\text{Re}\chi > 0$ ). It was used that  $\vec{f}_n^{fr,\omega} = -\gamma^{\omega} \vec{v}_n^{\omega}$ .

In the continuum approximation

$$\vec{f}_n^{ch} \rightarrow 3k_B T a^{-2} \partial^2 \vec{r}(t, n) / \partial n^2$$

( $a$  – mean square distance between beads along the chain)

Linearization: preaveraging the Oseen tensor over the equilibrium distribution.

Then  $\beta = \alpha$ ,

$$\langle H_{\alpha\beta nm}^{\omega} \rangle_0 = \delta_{\alpha\beta} h^{\omega}(n - m)$$

( $h^{\omega}$  is obtained exactly), and the normal modes can be defined,

$$\vec{r}^{\omega}(n) = \vec{r}_T^{\omega} + 2 \sum_{p=1}^{\infty} \vec{r}_p^{\omega} \cos(\pi n p / N).$$

The sum over  $n$  is replaced by the integral  $\int_0^N dn(\cdot)$

Small terms  $h_p^\omega = \int_0^N dn \int_0^N dm h^\omega(n-m)$  for  $p > 0$  are neglected.

This allows relating the CI coordinate to the random force,

$$r_{T\alpha}^\omega = \alpha(\omega) f_\alpha^\omega = - \left[ m\omega^2 + i\omega \left( \frac{h_0^\omega}{N} + \frac{1}{\gamma^\omega} \right)^{-1} \right]^{-1} f_\alpha^\omega,$$

$\alpha$  – susceptibility.

With the use of the fluctuation-dissipation theorem time correlation functions can be calculated.

For the motion of CI the MSD

$$X_T(t) = 2 \langle x_T(0)x_T(0) - x_T(0)x_T(t) \rangle \quad (x_T = r_{T\alpha})$$

is

$$X_T(t) = \frac{2k_B T}{\pi i} \int_{-\infty}^{\infty} \frac{\alpha(\omega)}{\omega} (1 - \cos \omega t) d\omega.$$

From here, various approximate results can be obtained.

For example, the long-time limit for Zimm polymers with  $h_0^0 \gamma \gg N$  is

$$X_T(t) \approx 2D_Z \left[ t - \left( \frac{3N\rho}{32\eta} \right)^{1/2} t^{1/2} + \dots \right] = 2D_Z t \left[ 1 - \frac{2}{\sqrt{\pi}} \left( \frac{\tau_R}{t} \right)^{1/2} + \dots \right],$$

where

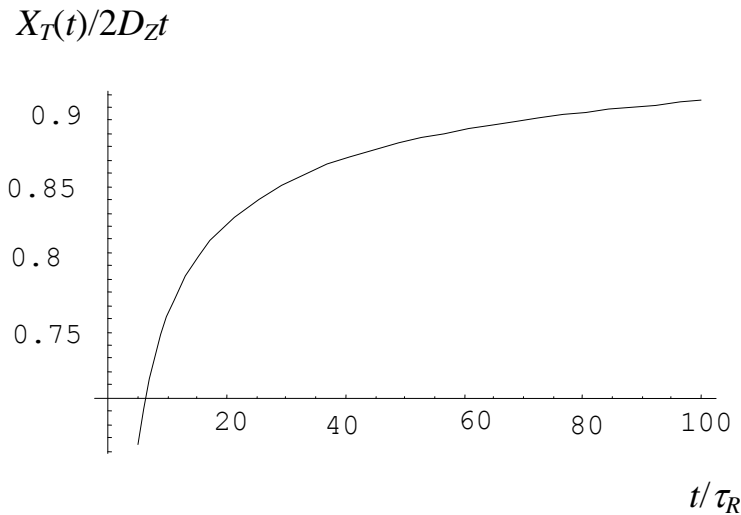
$$D_Z = k_B T h_0^0 N^{-2} = 8k_B T / 3\sqrt{6\pi^3 N \eta a}$$

is the diffusion coefficient known from the Zimm theory, and  $R$  in  $\tau_R = R^2 \rho / \eta$  is the hydrodynamic radius of the coil.

Again, in addition to the Einstein term we have the long-time tail  $\sim t^{1/2}$  (this is in agreement with, e.g., the computer simulations by C.P. Lowe et al.)

Thus the convergence to the classical result is slow:

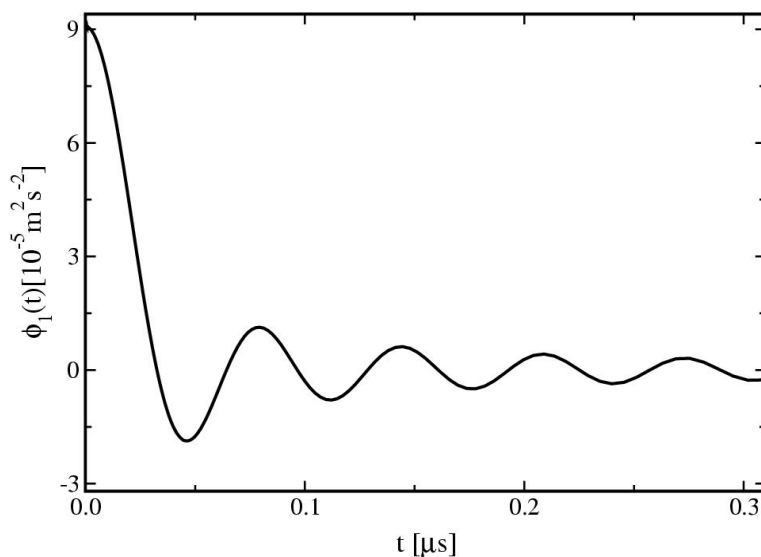




Additional result: For arbitrary strengths of the HI the diffusion coefficient of the coil contains both the Rouse and Zimm contributions,  $D_C = D_Z + D_R$  [10], where  $D_R = k_B T / N\gamma$ .

This could be important for interpretations of experiments.

**Internal modes**  $r_{p\alpha}^\omega$  are obtained in a similar way.



VAF for the  $p = 1$  mode. In the previous theory  $\text{VAF} < 0$  and monotonically relaxed to 0. That curve is on the graph indistinguishable from 0.

The internal modes do not relax exponentially:

Their correlation functions at long time contain “tails”, the longest lived being

$\sim t^{-5/2}$  (in the Zimm limit), in the Rouse case  $\sim t^{-3/2}$ .

### Relation to experiment

Suitable experiments seem to be scattering of light and neutrons, optical trapping, viscosimetry, NMR relaxometry...

The dynamic structure factor and its first cumulant  $\Gamma = -\frac{1}{G(k,0)} \frac{\partial G}{\partial t} \Big|_{t=t_0}$  are in qualitative agreement with experiments.

### Further developments?

- Equilibrium distribution can be non-Gaussian (the force  $\vec{f}_n^{ch}$  will change): shorter chains are less Gaussian.
- Volume interactions should be taken into account.
- Approximations done should be better substantiated.

## Appendices

### A. Evaluation of the nonstationary Oseen tensor

To take the hydrodynamic interactions into account, the equation of motion (1) with the friction force (2) has to be solved together with the hydrodynamic (Navier-Stokes and continuity) equations for the macroscopic velocity of the liquid,

$$\rho \frac{\partial \vec{v}}{\partial t} = -\nabla p + \eta \Delta \vec{v} + \vec{\phi}, \quad \text{div} \vec{v} = 0. \quad (\text{A1})$$

Here  $p$  is the pressure. The quantity  $\vec{\phi}$  has the meaning of an external force per unit volume [8]. Here

$$\vec{\phi}(\vec{r}) = -\sum_n \vec{f}_n^{fr}(\vec{r}_n) \delta(\vec{r} - \vec{r}_n). \quad (\text{A2})$$

The hydrodynamic equations (4) are solved using the Fourier transformation (FT)

$$\vec{v}_k^\omega = (2\pi)^{-4} \int d\vec{r} dt \exp\left[i(\vec{k}\vec{r} + \omega t)\right] \vec{v}(\vec{r}, t). \quad (\text{A3})$$

The solution,

$$\vec{v}_k^\omega = \frac{1}{k^2 \eta - i\omega \rho} \left[ \vec{\phi}_k^\omega - \frac{\vec{k}}{k^2} (\vec{k} \cdot \vec{\phi}_k^\omega) \right], \quad (\text{A4})$$

can be in the  $\vec{r}$ -representation, for any of the component  $\alpha$  ( $x$ ,  $y$ , or  $z$ ), written in the form

$$v_\alpha^\omega(\vec{r}) = \int d\vec{r}' \sum_\beta H_{\alpha\beta}^\omega(\vec{r} - \vec{r}') \phi_\beta^\omega(\vec{r}'). \quad (\text{A5})$$

The inverse transform, using (A2), is

$$v_\alpha(\vec{r}, t) = -\frac{1}{2\pi} \sum_{m, \beta} \int_{-\infty}^t dt' H_{\alpha\beta}^\omega(\vec{r} - \vec{r}_m, t - t') f_{m\beta}^{fr}(\vec{r}_m). \quad (\text{A6})$$

The Fourier transform of the Oseen tensor

$$H_{\alpha\beta}^{\omega}(\vec{r}) = \frac{1}{(2\pi)^3 \eta} \int \frac{d\vec{k}}{k^2 - i\omega\rho/\eta} \left( \delta_{\alpha\beta} - \frac{k_{\alpha}k_{\beta}}{k^2} \right) \exp(-i\vec{k}\vec{r}) \quad (\text{A7})$$

can be expressed as

$$H_{\alpha\beta}^{\omega}(\vec{r}) = A\delta_{\alpha\beta} + B \frac{r_{\alpha}r_{\beta}}{r^2}. \quad (\text{A8})$$

After the integration in (A7) we obtain

$$A = \frac{1}{8\pi\eta r} \left[ \exp(-y) - y \left( \frac{1 - \exp(-y)}{y} \right)'' \right],$$

$$B = \frac{1}{8\pi\eta r} \left[ \exp(-y) + 3y \left( \frac{1 - \exp(-y)}{y} \right)'' \right]. \quad (\text{A9})$$

Here  $y = r\chi$ ,  $\chi = \sqrt{-i\omega\rho/\eta}$  ( $\text{Re}\chi > 0$ ), and the prime denotes the differentiation with respect to  $y$ . Equations (A8) and (A9) can be used also in different problems on the dynamics of suspensions.

If the equilibrium distribution of the beads is Gaussian,

$$P(r_{nm}) = \left( \frac{3}{2\pi a^2 |n-m|} \right)^{3/2} \exp\left( -\frac{3}{2a^2} \frac{r_{nm}^2}{|n-m|} \right), \quad \vec{r}_{nm} \equiv \vec{r}_n - \vec{r}_m, \quad (\text{A10})$$

the preaveraging of the tensor (A8) consists in replacing it with the mean value over this distribution,

$$\langle H_{\alpha\beta nm}^{\omega} \rangle_0 = \left\langle A(r_{nm})\delta_{\alpha\beta} + B(r_{nm}) \frac{r_{nm\alpha}r_{nm\beta}}{r_{nm}^2} \right\rangle = \frac{\delta_{\alpha\beta}}{6\pi\eta} \left\langle \frac{1}{r_{nm}} \exp(-\chi r_{nm}) \right\rangle = \delta_{\alpha\beta} h^{\omega}(n-m) \quad (\text{A11})$$

The result of integration is

$$h^{\omega}(n-m) = \left( 6\pi^3 |n-m| \right)^{-1/2} (\eta a)^{-1} \left[ 1 - \sqrt{\pi} z \exp(z^2) \text{erfc}(z) \right],$$

$$z \equiv \chi a \sqrt{|n-m|/6}, \quad (\text{A12})$$

where  $\text{erfc}(\cdot)$  is the complementary error function. It is seen that the effective interaction between the beads decreases with the distance between the beads as

$$h^\omega(n-m) \approx \sqrt{\frac{3}{2\pi^2}} \frac{1}{-i\omega\rho a^2 |n-m|^{3/2}}, \quad |n-m| \rightarrow \infty,$$

i.e., more rapidly than in the case without memory when the function  $h$  at large  $|n-m|$  behaves as  $\sim |n-m|^{-1/2}$ .

Using (A12), the integral  $h_p^\omega = \int_0^N dn \int_0^N dm h^\omega(n-m) \cos(\pi pm/N)$  can be evaluated. Here we use it only at  $p=0$ , when

$$h_0^\omega = \frac{2N}{\pi\eta a^2 \chi} \left\{ 1 - \frac{2}{\sqrt{\pi} R_g \chi} - \frac{1}{(R_g \chi)^2} \left[ \exp(R_g^2 \chi^2) \text{erfc}(R_g \chi) - 1 \right] \right\} \quad (\text{A13})$$

( $R_g = a(N/6)^{1/2}$  is the gyration radius connected to the hydrodynamic radius  $R$  as  $Rg = 8R/(3\sqrt{\pi})$ ). At  $\omega \rightarrow 0$  we have

$$h_0^\omega \approx \frac{8N^{3/2}}{3\eta a \sqrt{6\pi^3}} \left( 1 - \frac{3\sqrt{\pi}}{8} R_g \chi + \dots \right), \quad (\text{A14})$$

and when  $\omega \rightarrow \infty$ ,

$$h_0^\omega \approx \frac{2N}{\pi\eta a^2 \chi} \left( 1 - \frac{2}{\sqrt{\pi} R_g \chi} + \frac{1}{(R_g \chi)^2} + \dots \right). \quad (\text{A15})$$

**B.** To determine the force  $\vec{f}_n^{ch}$  we use that the particles in the chain are arranged according to the Gauss law. This means that the probability for a particle to be in the position  $\vec{x}$  and another one in  $\vec{x}'$  is given by the correlation function

$$g(\vec{x}, \vec{x}') \sim \exp\left[-3(\vec{x} - \vec{x}')^2 / 2a^2\right], \quad (\text{B1})$$

where  $a$  is the mean square distance between them. Since from the statistical physics it follows for  $g(\vec{x}, \vec{x}')$

$$g(\vec{x}, \vec{x}') \sim \exp(-U/k_B T), \quad (\text{B2})$$

where  $U$  is the energy of interaction, we obtain

$$U = -k_B T \ln g(\vec{x}, \vec{x}') + \text{const.} \quad (\text{B3})$$

The whole interaction energy will be

$$U = \frac{3k_B T}{2a^2} \sum_{n=1}^{N-1} (\vec{x}_{n+1} - \vec{x}_n)^2 + A, \quad (\text{B4})$$

$A$  is independent on the conformation of the macromolecule.

The force  $f_n^{ch}$  ( $n \neq 1, N$ ):

$$\vec{f}_n^{ch} = -\frac{\partial U}{\partial \vec{x}_n} = \frac{3k_B T}{a^2} (\vec{x}_{n+1} + \vec{x}_{n-1} - 2\vec{x}_n).$$

The first and last particles have only one neighbor, so that

$$\vec{f}_1^{ch} = \frac{3k_B T}{a^2} (\vec{x}_2 - \vec{x}_1), \quad \vec{f}_N^{ch} = \frac{3k_B T}{a^2} (\vec{x}_{N-1} - \vec{x}_N).$$

For processes at the distances  $\gg$  size of monomers and for long chains ( $L \gg a$ ) the continuum approximation can be used:

$$x_n \rightarrow x(n, t), \quad x_{n\pm 1}(t) \rightarrow x(t, n) \pm \frac{\partial x(t, n)}{\partial n} + \frac{1}{2} \frac{\partial^2 x(t, n)}{\partial n^2} + \dots$$

Then the right sides of the equations will be

$$\begin{aligned} \dots &= \frac{3k_B T}{a^2} (x_2 - x_1) + f_1(t), & \dots &= \frac{3k_B T}{a^2} (x_{N-1} - x_N) + f_N(t), \\ & & \dots &= \frac{3k_B T}{a^2} (x_{n+1} + x_{n-1} - 2x_n) + f_n(t) \end{aligned}$$

We introduce fictive particles „0“ and „ $N + 1$ “, for which  $x_0 - x_1 \equiv 0$ ,  $x_{N+1} - x_N \equiv 0$ .)

In the continuum limit this is equivalent to the boundary conditions

$$\frac{\partial x(t, n)}{\partial n} = 0 \quad \text{for } n = 0, n = N.$$

---

Chain conformation is also affected by solvent quality. The intermolecular interactions between polymer chain segments and coordinated solvent molecules have an associated energy of interaction which can be positive or negative. For a *good solvent*, interactions between polymer segments and solvent molecules are energetically favorable, and will cause polymer coils to expand. For a *poor solvent*, polymer-polymer self-interactions are preferred, and the polymer coils will contract. The quality of the solvent depends on both the chemical compositions of the polymer and solvent molecules and the solution temperature.

If a solvent is precisely poor enough to cancel the effects of excluded volume expansion, the **theta ( $\theta$ ) condition** is satisfied. For a given polymer-solvent pair, the theta condition is satisfied at a certain temperature, called the **theta ( $\theta$ ) temperature** or **theta point**. A solvent at this temperature is called a theta solvent.

Below theta  $T$  - attraction between polymer segments, higher  $T$  - polymer expansion.

Theta  $T$  - second virial coeff- = 0.

Virial coefficients - in expansion of pressure of many-particle systems in powers of the density.